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INVERSION BETWEEN SPHALERITE- AND WURTZITE-TYPE STRUCTURES IN THE SYSTEM Zn–Fe–Ga–S

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ABSTRACT

The inversion between sphalerite and wurtzite in the system Zn–Fe–Ga–S was investigated by dry synthetic phase-equilibrium experiments. In the projection diagrams of the ZnS–FeS–GaS pseudoternary system at 900° and 800°C, the $(Zn,Fe,Ga)_{1-x}S$ solid solution extends over an extensive region from the ZnS composition toward both FeS- and GaS-compositions. At 900°C, this solid solution has the sphalerite structure along the ZnS–FeS join, consists of a mixture of sphalerite + wurtzite where there is a small amount of GaS component, and adopts the wurtzite structure where there is a greater proportion of the GaS and FeS components. A mixed sphalerite + wurtzite type occurs in the GaS-rich portion of the ZnS–GaS join and slightly extending toward the FeS composition. At 800°C, there is a similar distribution of polymorphs within the solid-solution field, except that the mixed sphalerite + wurtzite field is more extensive and includes the entire ZnS–GaS join. Heating experiments show that the inversion from the sphalerite structure to the wurtzite structure for a sample having composition $(ZnS)_{70}(GaS)_{30}$ occurs near 875°C. Reaction rates of this inversion are slow in both directions; the inversion temperature depends on the bulk composition (especially the concentration of cations) and the sulfur fugacity.

Keywords: inversion, sphalerite, wurtzite, system Zn–Fe–Ga–S, solid solution, phase equilibrium, dry synthesis.

SOMMAIRE

Nous avons étudié l'inversion entre la sphalérite et la wurtzite dans le système Zn–Fe–Ga–S au moyen de synthèses à sec. Dans les sections isothermes du système pseudoternaire à 900° et à 800°C, la solution solide $(Zn,Fe,Ga)_{1-x}S$ s'étend sur un large intervalle de composition, de ZnS vers FeS et GaS. A 900°C, cette solution solide adopte la structure de la sphalérite entre ZnS et FeS, un mélange des structures de sphalérite + wurtzite où la composition contient un peu de GaS, et la structure de la wurtzite où les compositions contiennent davantage de GaS et de FeS. On trouve aussi un champ de stabilité des structures sphalérite + wurtzite dans le secteur enrichi en GaS entre ZnS et GaS, qui s'étend légèrement dans la direction de FeS. A 800°C, nous trouvons une répartition semblable des structures dans le champ de solution solide, sauf que le domaine à sphalérite + wurtzite a une plus grande étendue et inclut l'intervalle ZnS–FeS au complet. Un chauffage de la composition $(ZnS)_{70}(GaS)_{30}$ mène à l'inversion de la structure de la sphalérite à la structure de la wurtzite près de 875°C. Les taux de réaction sont lents dans les deux directions. La température de l'inversion dépend de la composition du mélange, particulièrement la concentration des cations, et la fugacité du soufre.

(Traduit par la Rédaction)

Mots-clés: inversion, sphalérite, wurtzite, système Zn–Fe–Ga–S, solution solide, équilibre de phases, synthèse à sec.

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INTRODUCTION

Sphalerite is a cubic (3*C*) phase with the space group $F\bar{4}3m$, and wurtzite is a hexagonal (2*H*) phase with the space group *C6mc*. Various schemes of stacking of the 3-layer cubic and 2-layer hexagonal structures result in polytypism in pure ZnS (Smith 1955, Scott & Barnes 1972). However, synthetic phases in the system Zn–Fe–Ga–S contain only the end-member 3*C* sphalerite and 2*H* wurtzite structures. The former is the low-temperature phase, and the latter is the phase stable at high temperature. Ga- and Fe-bearing compositions of zinc sulfide are therefore phases of great interest to investigate 3*C*–2*H* stability relations. In this paper, we investigate the inversion between sphalerite-type and wurtzite-type structures, based on new experiments, on the results of our previous phase-equilibrium studies on portions of the system Zn–Fe–Ga–S (Ueno & Scott 1991, 1994, 1995), and on heating experiments of samples with composition $(ZnS)_{70}(GaS)_{30}$.

According to the previous work (Allen & Crenshaw 1912), the inversion temperature for pure ZnS is near 1020°C at 1 atm. However, attempts by some investigators to reproduce the 1020°C inversion have been unsuccessful, and both sphalerite and wurtzite have been synthesized over a wide range of temperatures (Scott & Barnes 1972). In the system Fe–Zn–S (Kullerud 1953, Barton & Toulmin 1966), the inversion temperature was found to decrease with increasing FeS content in the (Zn, Fe)S solid solution, to values as low as 850° – 875°C at 56 mol.% FeS, the maximum amount of Fe in this solid solution. Scott & Barnes (1972) argued, on the basis of rapid reaction-kinetics in hydrothermal systems, that wurtzite was not metastably formed in all low-temperature ores (*e.g.*, Mississippi-Valley-type deposits) and insisted that natural wurtzite must be stable under conditions far below 1020°C. Moreover, on the basis of their dry synthesis and hydrothermal experiments, they proposed that the inversion temperature is a function of sulfur fugacity, with sphalerite being the S-rich phase ($Zn_{1-x}S$), and wurtzite, the S-poor phase (ZnS_{1-x}). They found that the inversion of sphalerite to wurtzite proceeds much more slowly than the reverse reaction, which would likely lead to sphalerite rather than wurtzite stability where the two phases coexist at low temperatures.

TABLE 1. EXPERIMENTAL RESULTS FOR THE SYSTEM ZnS-FeS-GaS AT 900°C

Run no.	Reactants	Heating days	Products	Mol. % Sp in mixture
T027	ZnS+2GaS	22	Sp+GaS+Ga	
T039	ZnS+FeS+GaS	13	Wz+Y	
T047	ZnS+GaS	19	Sp(Wz)+Ga	88.4
T050	FeS+GaS	24	X+Z+Y	
T064	FeS+9GaS	21	GaS+Z+Y	
T065	3FeS+7GaS	21	GaS+Z+Y	
T066	7FeS+3GaS	21	X+Po+Y	
T067	9FeS+GaS	21	X+Po+Y	
T068	7ZnS+3GaS	23	Wz+Ga	
T069	9ZnS+GaS	23	Wz(Sp)+Ga	48.1
T150	ZnS+FeS+2GaS	19	V+Y	
T151	ZnS+FeS+4GaS	19	V+GaS+Y	
T152	ZnS+FeS+6GaS	19	V+GaS+Y	
T153	ZnS+FeS+8GaS	19	GaS+V+Y	
T154	2ZnS+2FeS+GaS	20	Wz+Y	
T155	4ZnS+4FeS+GaS	20	Wz+Y	
T156	ZnS+2FeS+GaS	20	Wz+Y	
T157	ZnS+4FeS+GaS	20	Wz+Po+Y	
T158	ZnS+6FeS+GaS	20	Wz+Po+Y	
T159	ZnS+8FeS+GaS	20	Po+Wz+Y	
T160	2ZnS+FeS+2GaS	20	Wz(Sp)+Y	46.3
T161	4ZnS+FeS+4GaS	20	Sp(Wz)+Y	63.7
T162	2ZnS+FeS+GaS	22	Wz+Y	
T163	4ZnS+FeS+GaS	22	Wz+Y	
T164	6ZnS+FeS+GaS	22	Wz+Y	
T165	8ZnS+FeS+GaS	22	Wz(Sp)+Y	11.4
T166	ZnS+2FeS+2GaS	22	Wz+V+Y	
T167	ZnS+4FeS+4GaS	22	Wz+V+Y	
T186	2ZnS+3GaS	23	Sp(Wz)+Ga	70.5
T195	ZnS+FeS+3GaS	18	V+Y	
T196	9ZnS+9FeS+22GaS	18	V+Y	
T197	11ZnS+11FeS+18GaS	18	Wz+Y	
T198	3ZnS+3FeS+4GaS	18	Wz+Y	
T205	ZnS+9FeS+10GaS	20	V+X+Y	
T206	ZnS+7FeS+12GaS	20	V+GaS+Y	
T207	ZnS+5FeS+14GaS	20	GaS+V+Y	
T208	ZnS+3FeS+16GaS	20	GaS+V+Y	
T209	3ZnS+FeS+16GaS	20	GaS+Y+V	

Sp: Sphalerite, Wz: Wurtzite, Y: Alloy Y, X: Phase X, Z: Phase Z
U: Phase U, V: Phase V, Po: Pyrrhotite, Zn: zinc, S: sulfur, Ga: gallium
Sp(Wz): Mixed phases in which sphalerite predominates
Wz(Sp): Mixed phases in which wurtzite predominates

TABLE 2. EXPERIMENTAL RESULTS FOR THE SYSTEM ZnS-FeS-GaS AT 800°C

Run no.	Reactants	Heating days	Products	Mol. % Sp in mixture
T028	ZnS+2GaS	28	Sp(Wz)+GaS+Ga	63.7
T040	ZnS+FeS+GaS	29	Wz+Y	
T048	ZnS+GaS	31	Sp(Wz)+GaS+Ga	82.7
T051	FeS+GaS	30	Z+X+Y	
T059	FeS+9GaS	33	GaS+Z+Y	
T060	3FeS+7GaS	33	GaS+Z+Y	
T061	7FeS+3GaS	33	X+Po+Y	
T062	9FeS+GaS	33	X+Po+Y	
T070	7ZnS+3GaS	35	Sp(Wz)+Ga	80.4
T071	9ZnS+GaS	35	Sp(Wz)+Ga	59.5
T168	ZnS+FeS+2GaS	44	V+Y	
T169	ZnS+FeS+4GaS	44	V+GaS+Y	
T170	ZnS+FeS+8GaS	47	GaS+V+Y	
T171	2ZnS+2FeS+GaS	44	Wz+Y	
T172	4ZnS+4FeS+GaS	44	Wz(Sp)+Y	34.2
T173	ZnS+2FeS+GaS	44	Wz+Y	
T174	ZnS+4FeS+GaS	47	Wz+Po+Y	
T175	ZnS+8FeS+GaS	47	Po+Wz+Y	
T176	2ZnS+FeS+2GaS	47	Wz(Sp)+Y	41.4
T177	4ZnS+FeS+4GaS	47	Sp(Wz)+Y	83.0
T178	2ZnS+FeS+GaS	44	Wz+Y	
T179	4ZnS+FeS+GaS	47	Wz(Sp)+Y	28.0
T180	8ZnS+FeS+GaS	44	Sp(Wz)+Y	51.7
T181	ZnS+2FeS+2GaS	44	Wz+V+Y	
T182	ZnS+4FeS+4GaS	44	V+Wz+Y	
T199	ZnS+FeS+6GaS	40	GaS+V+Y	
T200	ZnS+FeS+3GaS	40	V+Y+GaS	
T201	9ZnS+9FeS+22GaS	40	V+Y	
T202	11ZnS+11FeS+18GaS	35	V+Y+Wz	
T203	3ZnS+3FeS+4GaS	35	V+Wz+Y	
T210	ZnS+9FeS+10GaS	40	V+X+Y	
T211	ZnS+7FeS+12GaS	40	GaS+V+Y	
T212	ZnS+5FeS+14GaS	40	GaS+V+Y	
T213	ZnS+3FeS+16GaS	40	GaS+V+Y	
T214	3ZnS+FeS+16GaS	40	GaS+U+V	

Sp: Sphalerite, Wz: Wurtzite, Y: Alloy Y, X: Phase X, Z: Phase Z
U: Phase U, V: Phase V, Po: Pyrrhotite, Zn: zinc, S: sulfur, Ga: gallium
Sp(Wz): Mixed phases in which sphalerite predominates
Wz(Sp): Mixed phases in which wurtzite predominates

Kojima & Ohmoto (1991) disagreed and proposed, on the basis of hydrothermal syntheses and the natural occurrence of wurtzite, that hydrothermal wurtzite is a metastable mineral formed by rapid precipitation from highly supersaturated solutions. Kojima (1991) carried out wurtzite–sphalerite inversion experiments using a solution-mediated method in the temperature range from 200° to 350°C, and found that the inversion rate of iron-rich wurtzite to sphalerite is slower than that of pure ZnS wurtzite, but is remarkably faster than the inversion in solid-state experiments. He also explained the presence of pseudomorphic sphalerite observed in modern ocean-floor deposits as a result of rapid inversion from wurtzite.

In addition to kinetics, the incorporation of several elements is known to profoundly affect the temperature of the sphalerite–wurtzite inversion. In hydrothermal experiments in the system ZnS–MnS, Tauson *et al.* (1977) showed that the inversion temperature decreases to 350°C at a composition $(ZnS)_{74}(MnS)_{26}$. In hydrothermal syntheses in the ternary system ZnS–MnS–CdS at 500°C and 1000 atm, Tauson & Chernyshev (1978) found that the ZnS-rich portion of this system has the sphalerite structure, the CdS-rich portion has the wurtzite structure, and the MnS-rich portion is a mixture of two phases, alabandite and wurtzite; sphalerite and wurtzite coexist on the boundaries between the single-phase regions. Maurel

TABLE 3. CHEMICAL COMPOSITION OF SPHALERITE, WURTZITE, PHASE Z, PHASE X AND PHASE V IN EXPERIMENTS ALONG THE JOIN ZnS-FeS-GaS AT 900°C

Run no.	Phase	Weight %					Mol. %		
		Zn	Fe	Ga	S	Total	ZnS	FeS	GaS
T027	Sp	27.6	0.0	36.6	36.9	101.1	44.7	0.0	55.3
T039	Wz	25.0	16.1	22.0	37.0	100.1	38.8	29.3	31.9
T047	Sp	36.6	0.0	27.4	36.1	100.1	58.7	0.0	41.3
T050	Z	0.0	16.7	42.7	40.9	100.3	0.0	32.9	67.1
	X	0.0	27.4	32.6	40.3	100.3	0.0	51.3	48.7
T065	Z	0.0	16.5	42.5	40.7	99.7	0.0	32.7	67.3
T066	X	0.0	27.5	32.3	40.6	100.4	0.0	51.4	48.6
T067	X	0.0	27.4	32.6	40.3	100.3	0.0	51.3	48.7
T068	Wz	49.1	0.0	16.5	34.3	99.9	76.0	0.0	24.0
T069	Wz	62.9	0.0	3.8	33.5	100.2	94.7	0.0	5.3
T150	V	16.3	5.1	39.8	39.5	100.7	27.3	10.1	62.6
T151	V	14.7	3.7	41.9	39.2	99.5	25.1	7.3	67.3
T152	V	16.2	3.1	41.2	38.6	99.1	27.7	6.3	66.2
T153	V	16.6	3.4	39.8	38.8	98.6	28.7	6.9	64.4
T154	Wz	29.3	22.6	12.2	35.8	99.9	43.6	39.5	16.9
T155	Wz	32.6	25.3	6.4	35.2	99.5	47.9	43.3	8.8
T156	Wz	18.1	29.3	16.4	35.2	99.0	26.8	50.6	22.6
T157	Wz	17.5	34.0	12.6	35.5	99.6	25.4	57.6	17.0
T158	Wz	16.9	34.3	12.6	35.2	98.8	24.3	58.5	17.2
T159	Wz	18.0	32.0	12.9	35.8	98.7	26.6	55.5	17.9
T160	Wz	29.6	6.2	27.3	35.7	98.8	47.4	11.7	40.9
T161	Sp	37.4	0.4	25.4	36.6	99.8	60.6	0.7	38.7
T162	Wz	35.6	12.5	15.9	35.1	99.1	54.6	22.5	22.9
T163	Wz	46.9	8.1	9.9	34.1	99.0	71.4	14.4	14.2
T164	Wz	52.1	5.2	7.8	35.0	100.1	79.5	9.4	11.1
T165	Wz	55.7	5.0	5.1	34.6	100.4	83.9	8.9	7.2
T166	Wz	13.8	19.0	28.2	38.7	99.7	22.2	35.5	42.3
	V	10.5	10.2	39.3	38.7	98.7	17.7	20.0	62.2
T167	W	10.0	22.2	29.9	38.8	100.9	15.7	40.5	43.8
	V	9.3	12.0	41.2	39.6	102.1	15.0	22.6	62.4
T186	Sp	30.4	0.0	31.8	37.1	99.3	50.6	0.0	49.4
T195	V	16.8	3.1	41.9	38.7	100.5	28.1	6.0	65.9
T196	V	16.8	3.8	40.3	39.2	100.1	28.5	7.5	64.0
T197	Wz	24.2	9.2	29.1	35.8	98.3	38.9	17.2	43.9
T198	Wz	23.3	10.5	28.0	36.9	98.7	37.7	20.0	42.3
T205	V	4.8	14.9	40.4	39.0	99.1	7.9	29.1	63.0
	X	1.7	25.9	33.1	38.7	99.4	2.7	48.2	49.1
T206	V	4.6	12.9	41.4	41.0	99.9	8.0	25.7	66.3
T207	V	5.4	11.4	42.7	40.7	100.2	9.2	22.7	68.1
T208	V	13.2	5.6	41.2	41.5	101.5	22.5	11.3	66.2
T209	V	21.2	2.1	35.8	39.6	98.7	37.1	4.3	58.6

Sp: sphalerite, Wz: wurtzite, Z: Phase Z, X: Phase X, V: Phase V

TABLE 4. CHEMICAL COMPOSITION OF SPHALERITE, WURTZITE, PHASE Z, PHASE X AND PHASE V IN EXPERIMENTS ALONG THE JOIN ZnS-FeS-GaS AT 800°C

Run no.	Phase	Weight %					Mol. %		
		Zn	Fe	Ga	S	Total	ZnS	FeS	GaS
T028	Sp	40.3	0.0	23.8	36.3	100.4	64.4	0.0	35.6
T040	Wz	25.4	15.3	21.9	36.9	99.5	39.7	28.1	32.2
T051	Z	0.0	16.9	43.1	40.3	100.3	0.0	32.9	67.1
	X	0.0	26.9	32.7	40.3	99.9	0.0	50.6	49.4
T060	Z	0.0	16.7	43.0	40.2	99.9	0.0	32.7	67.3
T061	X	0.0	27.0	32.3	40.5	99.8	0.0	50.9	49.1
T070	Sp	50.6	0.0	14.7	34.8	100.1	78.6	0.0	21.4
T071	Sp	62.5	0.0	3.6	33.4	99.5	94.9	0.0	5.1
T168	V	17.3	4.7	39.5	37.1	98.6	29.0	9.3	61.8
T169	V	17.1	3.1	42.1	38.7	101.0	28.4	6.0	65.6
T171	Wz	31.5	21.5	11.0	37.4	101.4	47.0	37.6	15.4
T172	Wz	32.6	26.3	5.9	34.9	99.7	47.4	44.7	7.9
T173	Wz	17.9	28.4	17.1	36.4	99.8	26.7	49.5	23.8
T174	Wz	16.3	31.6	15.3	35.5	98.7	24.0	54.7	21.3
T175	Wz	16.1	30.9	15.3	36.9	99.2	24.3	54.2	21.5
T176	Wz	32.6	3.5	27.2	37.9	101.2	52.5	6.5	41.0
T177	Sp	34.8	1.8	26.1	38.2	100.9	56.7	3.4	39.9
T178	Wz	36.4	13.7	14.8	36.5	101.4	55.0	24.2	20,8
T179	Wz	45.4	7.4	10.7	35.2	98.8	70.8	13.5	15.7
T180	Sp	57.5	4.4	3.5	33.1	98.5	87.2	7.9	4.9
T181	Wz	13.7	21.4	25.2	37.7	98.0	21.9	40.2	37.9
T182	Wz	9.5	24.5	27.7	38.1	99.8	14.8	44.7	40.5
	V	6.8	13.4	40.5	39.1	99.8	11.1	26.0	62.9
T199	V	17.6	2.2	39.8	40.2	99.8	30.6	4.4	65.0
T200	V	16.2	3.3	40.7	39.4	99.6	27.8	6.7	65.5
T201	V	17.5	4.0	38.0	39.2	98.7	30.2	8.1	61.7
T202	V	16.2	6.5	36.8	39.2	98.7	27.7	13.0	59.3
	Wz	27.7	9.2	25.7	37.1	99.7	44.4	17.2	38.4
T203	Wz	26.1	9.6	25.5	38.3	99.5	42.5	18.4	39.1
T210	X	1.1	26.7	30.9	40.5	99.2	1.9	50.9	47.2
T211	V	3.5	14.2	40.5	40.0	98.2	6.0	28.6	65.4
T212	V	6.0	11.4	41.3	40.4	99.1	10.4	22.9	66.7
T213	V	9.2	9.7	40.4	40.5	99.8	15.7	19.3	65.0
T214	U	9.2	0.4	58.0	32.1	99.7	14.3	0.8	84.8

Sp: sphalerite, Wz: wurtzite, Z: Phase Z, X: Phase X, V: Phase V

(1978) investigated the stability of sphalerite and wurtzite in the system Zn–Cd–S, and found that sphalerite is the only stable phase if the amount of CdS is less than 12.2 mol.% at 650°C, 10.3% at 730°C and 7.6% at 800°C, wurtzite is the only stable phase if this amount is greater than 14.3 mol.% at 650°C, 11.5% at 730°C and 9.2% at 800°C, and between these limits, both phases coexist. Shima *et al.* (1982) studied the phase relations around sphalerite solid-solution in the system Cu–Fe–Zn–S and Mn–Fe–Zn–S, and found that manganese-bearing wurtzite is stable at temperatures as low as 350°C, with a broad solid-solution area in the central part of the ternary system FeS–ZnS–MnS. Osadchii (1991) performed hydrothermal experiments in the system Cu_2SnS_3–ZnS–CdS at 400°C and 101.3 MPa and showed that three solid-solutions exist with wide fields of stability: kesterite–Černýite, sphalerite and wurtzite (greenockite) are defined within the whole range of compositions. Kubo *et al.* (1992) investigated the distribution of Zn, Fe, Mn and Cd between sphalerite and aqueous chloride solution at 400° and 600°C and 1 kbar under relatively reducing conditions, and showed that the elements are preferentially partitioned into sphalerite in the order Cd > Zn > Fe > Mn. Their experiments in the system Mn–Zn–S showed that the most MnS-rich part of the (Zn,Mn)S solid-solution (compositional range 21–26 mol.% MnS at 400°C and 13–44 mol.% MnS at 600°C) is a wurtzite-type solid-solution. These observations mean that FeS, MnS and CdS in solid solution in zinc sulfide considerably decrease the inversion temperature.

EXPERIMENTAL

Following Ueno & Scott (1991, 1994, 1995), dry-synthesis equilibrium experiments in the system Zn–Fe–Ga–S were performed in evacuated silica tubes. Three elements (Fe, Ga and S), all of 99.99% purity or better, were used to synthesize the starting materials, FeS and GaS. ZnS was used as a commercially available white, powdered reagent, in wurtzite form. The experiments in this study focused mainly on the pseudoternary system ZnS–FeS–GaS. Additional data are from phase diagrams at 900° and 800°C of the systems Fe–Ga–S (Ueno & Scott 1994) and Zn–Ga–S (Ueno & Scott 1995) and of the system Zn–Fe–S (Barton & Toulmin 1966). In order to investigate the change of inversion rate between sphalerite and wurtzite with temperature, heating experiments were performed between 750° and 900°C at 25°C intervals using a bulk composition of $(ZnS)_{70}(GaS)_{30}$. The reason for choosing this composition is that an experiment at 900°C showed wurtzite + Ga (T068 in Table 1) and an experiment at 800°C showed sphalerite + wurtzite + Ga (T070 in Table 2). After quenching in water, all products were examined by reflected-light microscopy and by X-ray powder diffractometry (Mac Science high-energy X-ray diffractometer) and electron-microprobe analysis (JEOL 50A). Operating conditions for the microprobe were 25 kV and 20 nA (on MgO crystal). Synthetic ZnS, FeS, GaS and Ga_2S_3 were used as standards. All analytical errors were found to be within 0.1 wt.%.

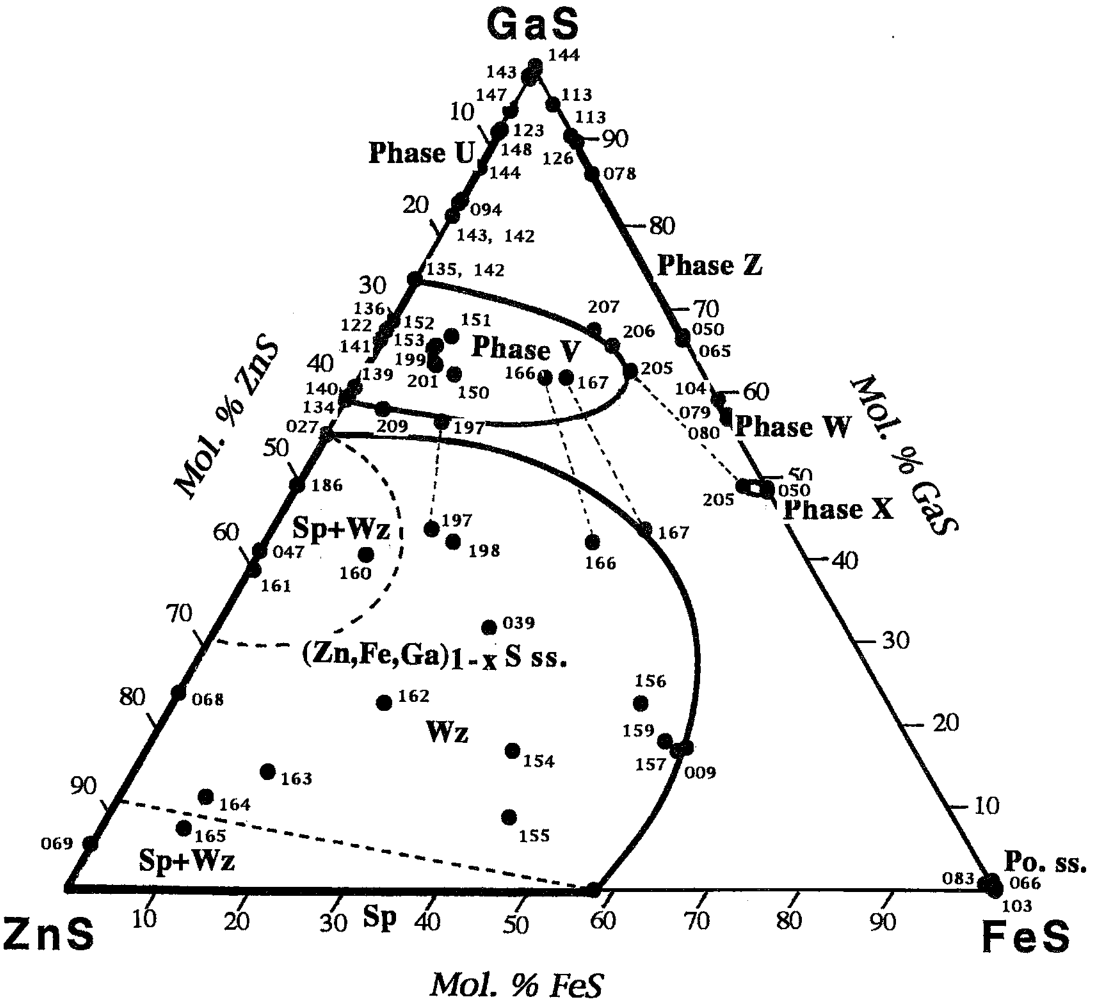

FIG. 1. Isothermal section through the system ZnS–FeS–GaS at 900°C.

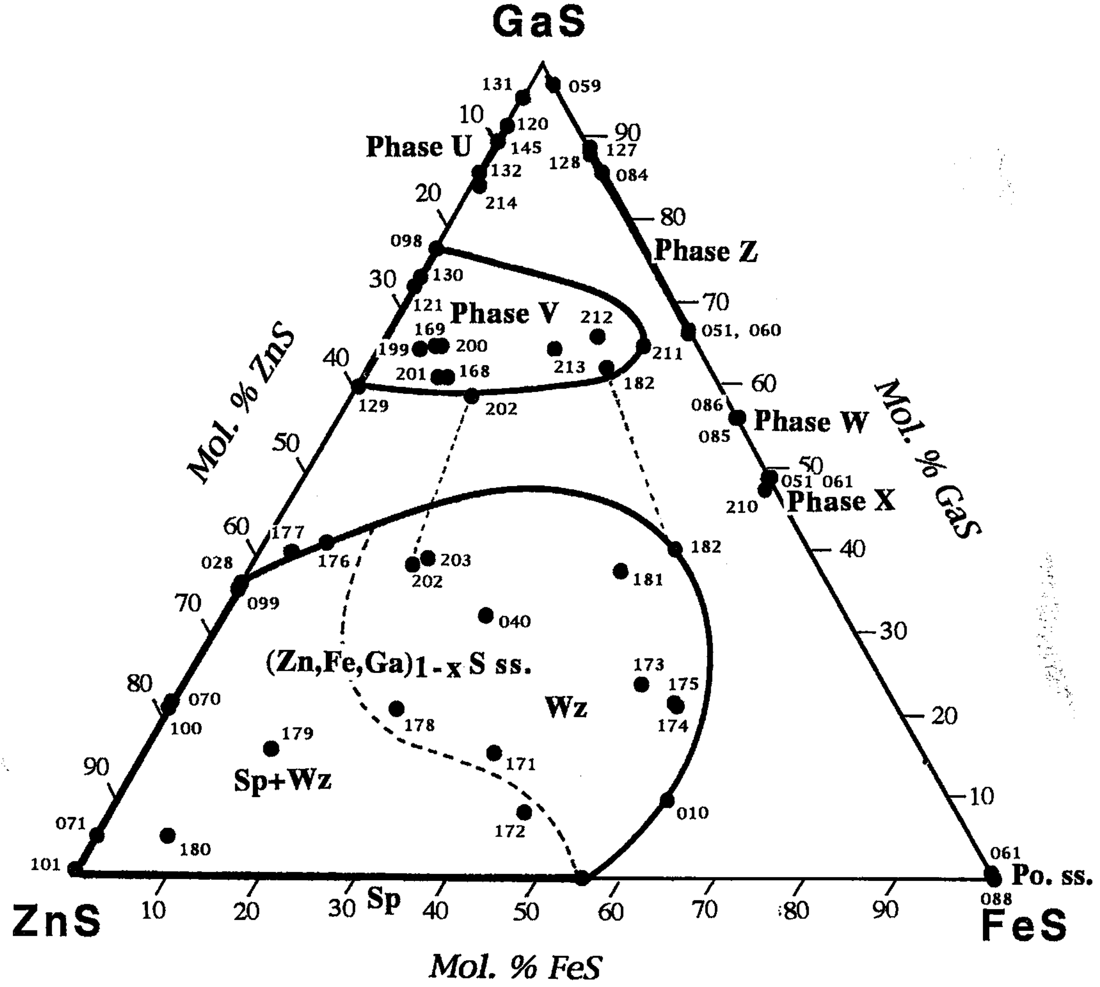

FIG. 2. Isothermal section through the system ZnS–FeS–GaS at 800°C.

RESULTS AND DISCUSSION

The system ZnS–FeS–GaS at 900° and at 800°C

The results of our phase-equilibrium experiments in the ternary system ZnS–FeS–GaS at 900° and at 800°C are reported in Tables 1 and 2, respectively. Run periods were 13–24 days at 900°C and 28–47 days at 800°C. Products are listed in order of relative abundance. In the case of mixtures of sphalerite-type and wurtzite-type phases, the mol.% of the sphalerite-type phase was calculated using an equation from Ueno & Scott (1995). Alloy *Y* is a binary tetragonal alloy of Fe and Ga described by Ueno & Scott (1991). *W* is a hexagonal phase in the system Ga–Fe–S, described by Ueno & Scott (1994). *X* and *Z* are phases in the system Ga–Fe–S, described by Ueno & Scott (1994), and are tetragonal and cubic, respectively. *V* and *U* are phases in the system Zn–Ga–S described by Ueno & Scott (1995), and also are tetragonal and cubic, respectively. Results of chemical analyses of the sphalerite-type phase, wurtzite-type phase, phase Z, phase *X* and phase *V* at 900° and at 800°C are listed in Tables 3 and 4, respectively. These analytical values are averages of several grains. All the sulfide grains analyzed contain more than 50 atomic % sulfur. In order to plot these on a ternary plane of the system ZnS–FeS–GaS, the atomic percentages of Zn, Fe and Ga were calculated in

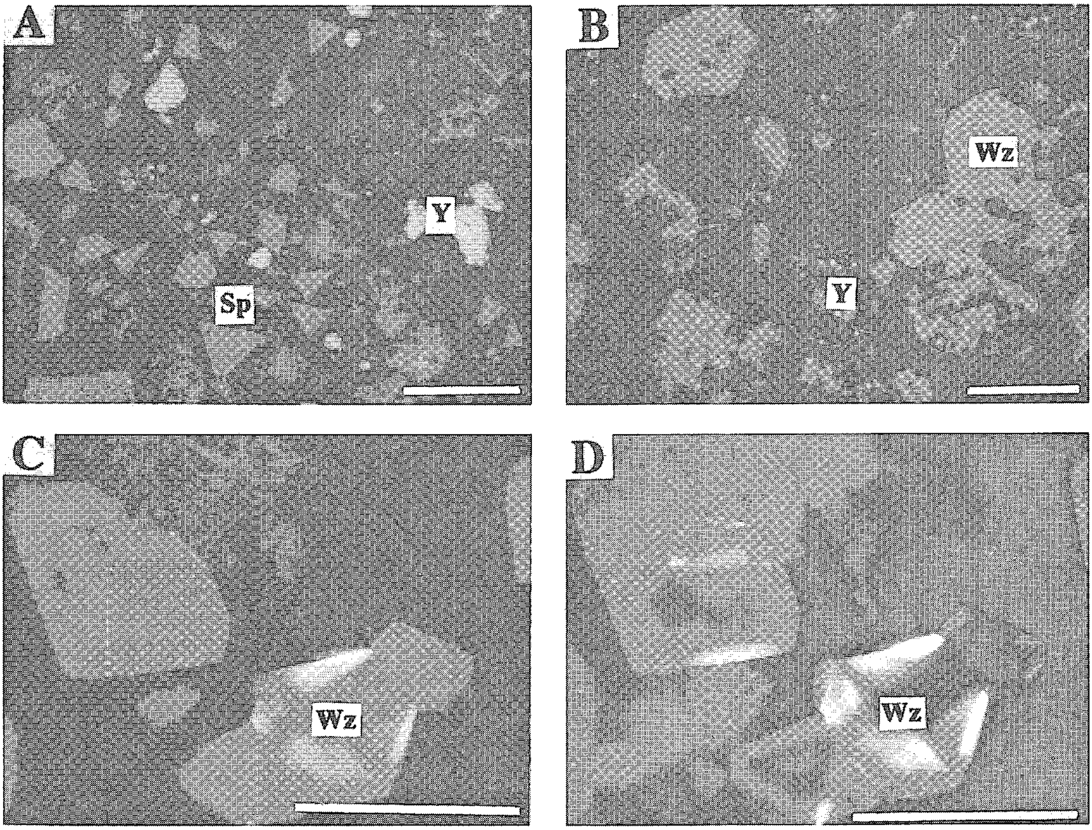

FIG. 3. Photomicrographs in reflected light. (A) Sphalerite (Sp) + alloy *Y* (Y); (B) wurtzite (Wz) + alloy *Y* (Y); (C, D) polyhedral crystals of wurtzite, with uncrossed and crossed nicols, respectively. Matrix is resin in all photos. Scale bars are 100 μm in A and B, and 50 μm in C and D.

terms of normalized molar percentages of ZnS, FeS and GaS. The resulting pseudoternary projections of the system ZnS–FeS–GaS at 900° and at 800°C are shown in Figures 1 and 2, respectively. The solid points in the figures are the analytical values expressed as normalized mol.%, and the small numbers show run numbers. The join ZnS–FeS is taken from Barton & Toulmin (1966), and the joins FeS–GaS and GaS–ZnS are from Ueno & Scott (1994 and 1995, respectively). All phases, except *W* and *X*, are moderate to extensive binary or ternary solid-solutions. Sphalerite and wurtzite have broad solid-solution areas: the maximum Ga contents are 24.9 at.% at 900°C (run T027) and 18.3 at.% at 800°C (run T182), and maximum Fe contents are 28.6 at.% at 900°C (run T158) and 26.4 at.% at 800°C (run T174).

As gallium is both a divalent and a trivalent element, it dissolves as GaS and Ga_2S_3 into the (Zn,Fe)S solid-solution in the system Zn–Fe–Ga–S. Ueno & Scott (1991) expressed this solid-solution as $(Zn,Fe,Ga)_{1-x}S$, to accommodate the presence of cation deficiencies. At 900°C (Fig. 1), this solid solution has the sphalerite structure along the ZnS–FeS join. Addition of only a small amount of GaS component to the solid solution results in the appearance of a mixture of sphalerite and wurtzite, and extensive incorporation of GaS component and FeS component stabilizes the wurtzite structure. The GaS-rich portion of the $(Zn,Fe,Ga)_{1-x}S$ solid solution on the join ZnS–GaS is of the mixed type and extends slightly to FeS-rich compositions. At 800°C (Fig. 2), the results are somewhat similar. The join ZnS–FeS of this solid solution has the sphalerite structure. The presence of more FeS component and more GaS component stabilizes the wurtzite structure. The join ZnS–GaS and the remaining area in this solid solution consist of mixtures of sphalerite and wurtzite. It is difficult to distinguish between sphalerite and wurtzite on the basis of microscope observations. The color of both phases in reflected light is gray. However, where euhedral crystals are obtained, they are easily identified. In polished sections, triangular forms indicate that the phase is sphalerite (Fig. 3A) and hexagonal forms indicate that the phase is wurtzite (Fig. 3B). In some cases, we obtained striking polyhedral crystals of wurtzite, (Figs. 3C, D) in our experiments on the system Zn–Fe–Ga–S, and showed some photos obtained by scanning electron microscopy in our previous papers (Ueno & Scott 1994, 1995).

Inversion experiments for $(ZnS)_{70}(GaS)_{30}$

Additional experiments were conducted to test whether the sphalerite phase in the sphalerite–wurtzite mixtures is metastable, as claimed for some natural occurrences by Scott & Barnes (1972). Two starting ZnS materials were prepared. One is commercially available 100% wurtzite, and the other is 100% sphalerite that had been inverted from wurtzite by heating for 7 days at 900°C. Both were examined by X-ray powder diffraction. Choosing $(ZnS)_{70}(GaS)_{30}$ as the bulk composition, heating experiments at progressively higher temperature were performed in 25°C steps from 750° to 900°C for 7 days and 25 days. The resulting ratios of sphalerite and wurtzite in the products are shown in Table 5. At 750°C, with wurtzite as the starting material, the abundance of sphalerite phase increased from 30.3% after 7 days of heating to 61.6% after 25 days of heating but, with sphalerite as the starting material, no wurtzite phase was formed after 7 days or 25 days of heating. These results mean that the sphalerite phase is stable at 750°C. The results at 775°, 800°, 825° and 850°C are similar to those at 750°C. At 875°C, a reversal was obtained in the phase that appears on heating. With wurtzite as the starting material, the proportion of sphalerite in the product increases from 12.5% after 7 days of heating and to 57.5% after 25 days but, with sphalerite as the starting material, the product was found to contain 75.3% sphalerite after 7 days of heating, and this decreased to 61.6% after 25 days. At 900°C, with wurtzite as the starting material, the wurtzite phase became 100% after 25 days of heating, and with sphalerite as the starting material, the proportion of sphalerite in the product decreased from 23.7% after 7 days of heating to 0% after 25 days.

Figure 4 illustrates the above results. From 750° to 850°C, the direction of the inversion is from wurtzite phase to the sphalerite phase. At 875°C, when using wurtzite as the starting material, the direction of the inversion is from wurtzite phase to the sphalerite phase and, with sphalerite as the starting material, it is from sphalerite phase to the wurtzite phase. Therefore, for the $(ZnS)_{70}(GaS)_{30}$ composition, we have shown that the sphalerite phase is stable below 850°C, and that at 875°C, wurtzite and sphalerite phases coexist.

TABLE 5. VARIATION OF THE PROPORTION OF SPHALERITE AND WURTZITE IN EXPERIMENTS TO DETERMINE INVERSION TEMPERATURE

Run no.	Bulk compositions (Mol. %)	Temp. (°C)	Heating days	Products	Sp-Wz ratio (Mol. % Sp)
T221	$(Wz)_{70}(GaS)_{30}$	750	7	Wz+Sp+GaS	30.3
T221'	$(Wz)_{70}(GaS)_{30}$	750	25	Sp+Wz+GaS	61.6
T228	$(Sp)_{70}(GaS)_{30}$	750	7	Sp+GaS+Ga	100.0
T228'	$(Sp)_{70}(GaS)_{30}$	750	25	Sp+GaS+Ga	100.0
T230	$(Wz)_{70}(GaS)_{30}$	775	7	Wz+Sp+GaS	34.2
T230'	$(Wz)_{70}(GaS)_{30}$	775	25	Sp+Wz+Ga	65.9
T227	$(Sp)_{70}(GaS)_{30}$	775	7	Sp+GaS+Ga	100.0
T227'	$(Sp)_{70}(GaS)_{30}$	775	25	Sp+GaS+Ga	100.0
T222	$(Wz)_{70}(GaS)_{30}$	800	7	Sp+Wz+GaS	44.7
T222'	$(Wz)_{70}(GaS)_{30}$	800	25	Sp+Wz+GaS	68.2
T223	$(Sp)_{70}(GaS)_{30}$	800	7	Sp+GaS+Ga	100.0
T223'	$(Sp)_{70}(GaS)_{30}$	800	25	Sp+GaS+Ga	100.0
T231	$(Wz)_{70}(GaS)_{30}$	825	7	Wz+Sp+GaS	46.3
T231'	$(Wz)_{70}(GaS)_{30}$	825	25	Sp+Wz+GaS	70.8
T224	$(Sp)_{70}(GaS)_{30}$	825	7	Sp+GaS+Ga	100.0
T224'	$(Sp)_{70}(GaS)_{30}$	825	25	Sp+GaS+Ga	100.0
T232	$(Wz)_{70}(GaS)_{30}$	850	7	Wz+Sp+Ga	49.9
T232'	$(Wz)_{70}(GaS)_{30}$	850	25	Sp+Wz+Ga	77.8
T225	$(Sp)_{70}(GaS)_{30}$	850	7	Sp+Ga	100.0
T225'	$(Sp)_{70}(GaS)_{30}$	850	25	Sp+Ga	100.0
T233	$(Wz)_{70}(GaS)_{30}$	875	7	Wz+Sp+Ga	12.5
T233'	$(Wz)_{70}(GaS)_{30}$	875	25	Sp+Wz+Ga	57.5
T226	$(Sp)_{70}(GaS)_{30}$	875	7	Sp+Wz+Ga	75.3
T226'	$(Sp)_{70}(GaS)_{30}$	875	25	Sp+Wz+Ga	61.6
T068	$(Wz)_{70}(GaS)_{30}$	900	25	Wz+Ga	0.0
T229	$(Sp)_{70}(GaS)_{30}$	900	7	Wz+Sp+Ga	23.7
T229'	$(Sp)_{70}(GaS)_{30}$	900	25	Wz+Ga	0.0

Sp: sphalerite, Wz: wurtzite

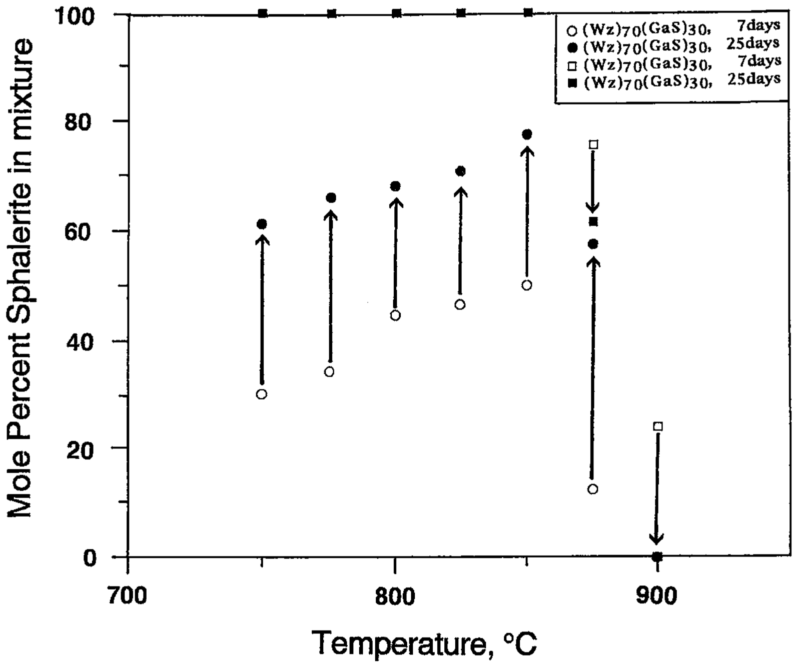

FIG. 4. Variation of the inversion ratio between sphalerite and wurtzite structures.

CONCLUDING REMARKS

We conclude, from these experiments, that the inversion between the sphalerite phase and wurtzite phase for a $(ZnS)_{70}(GaS)_{30}$ composition occurs near 875°C. Figures 1 and 2 drawn for the 900° and 800°C isotherms, respectively, show that the inversion temperature is strongly dependent on bulk composition. The inversion temperature decreases with increasing contents of additional metals (gallium and iron). This is similar to the experimental results of Barton & Toulmin (1966) for dry synthesis experiments in the system Zn–Fe–S, Tauson *et al.* (1977) for hydrothermal experiments in the system ZnS–MnS, Tauson & Chernyshev (1978) for hydrothermal experiments in the system ZnS–MnS–CdS–FeS, and Kubo *et al.* (1992) for hydrothermal experiments in the system Zn–Mn–S. Scott & Barnes (1972) concluded that sphalerite in the Zn–Fe–S system is stable at high sulfur fugacity, but in our experiments in the system Zn–Fe–Ga–S, we found that the wurtzite phase appears in the Ga-rich (S-rich) portion. Thus we conclude that the addition of other metallic elements into the solid solution lowers the inversion temperature; conversely, an increase of sulfur fugacity should raise it.

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